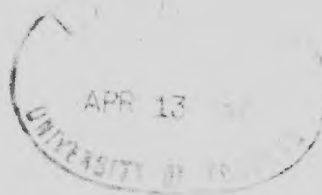


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**PAPERS FROM THE CHEMICAL
LABORATORIES**

**No. 103: RESEARCHES IN PHYSICAL CHEMISTRY, BY W.
LASH MILLER AND FRANK B. KENRICK**

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Researches in Physical Chemistry carried out in the University of Toronto,
VII.

Communicated by

PROF. W. LASH MILLER, and PROF. FRANK B. KENRICK, F.R.S.C.

(Read May 28, 1913)

No. 1. *Frank B. Kenrick*:—The hydrates and acid salts of ferrous sulphate. The compositions of a number of ferrous sulphates and their ranges of existence with sulphuric acid solutions at ordinary temperatures have been determined. The composition of the solid phase was obtained by a combination of two methods of indirect analysis, each of which alone was insufficiently accurate for the purpose. In the first method, the analyses of liquids and corresponding wet solids gave the values of a and b in a number of equations to straight lines:

$$y = ax + b \quad y = a^1x + b^1 \quad \text{etc.}$$

in which y represents the amount of ferrous oxide (FeO) and x the amount of water (H_2O) to unit quantity of sulphuric anhydride (SO_3), and the points on which correspond to possible compositions of the solid phase. In some cases the values of x and y representing the values of the actual solid, could be determined from the cutting point of these lines; in others the smallness of the angles made this impracticable. In the second method, each analysis of liquid and wet solid gave the value of y fairly accurately, although the value found for x was too inaccurate to be of any use. By combining the two methods and substituting the value of y given by the second method in any of the equations obtained by the first, the value of x could be determined.

The following chemical compounds were identified:— $FeO \cdot SO_3 \cdot H_2O$, stable in contact with solutions of composition varying from SO_3 : 2.186 H_2O to SO_3 : 7.93 H_2O at which point the heptahydrate was formed. $2FeO \cdot 3SO_3 \cdot 2H_2O$ (?) stable with solutions SO_3 : 1.637 H_2O to SO_3 : 2.186 H_2O . $FeO \cdot 2SO_3 \cdot H_2O$ existing with solutions SO_3 : 1.342 H_2O to (about) SO_3 : 1.595 H_2O . $FeO \cdot 4SO_3 \cdot 3H_2O$ stable with solutions ranging from strongest one investigated viz.:— SO_3 : 1.122 H_2O to about SO_3 : 1.342 H_2O . (*Jour. Phys. Chem.* 12, pp. 693-705, 1908).

No. 2. *W. Lash Miller and R. H. McPherson*:—The behaviour of colloidal suspensions with immiscible solvents. A study of the behaviour of colloidal suspensions of arsenious sulphide, etc., in different

solvents, with a view to discovering, if they exist, cases of equilibrium analogous to the distribution of iodine between ether and water. It seemed *a priori* probable that such equilibria would most likely be met with in the case of colloids with marked power of diffusion, and immiscible solvents which approach each other closely in properties and composition, such as those near the "critical solution temperature" in two-component systems, or the solutions near the plait-point of the binodal curve in three-component systems.

The Winkelblech effect (coagulation of the colloid at the boundary between the solvents) interfered with the observations in the case of silver hydrosol and phenol, amyl alcohol, or isobutyl alcohol; two experiments shewed the dependence of the Winkelblech effect on capillary forces.

Chloroform and alcohol did not coagulate the hydrosol of arsenious sulphide, but no distribution was observed even at the plait-point; this is not due to "passive resistance." The same is true when the alcohol was replaced by acetone; but if ether or ethyl acetate were substituted for the chloroform distribution readily occurred, whether alcohol, acetone or propyl alcohol was employed as consolute liquid. In this connection a rapid method of determining the binodal curve, tie-lines, and plait-point was worked out.

Antimony trisulphide, like the sulphide of arsenic, distributed between the two liquid phases in the system water-ether-alcohol; but not in the system water-chloroform-alcohol. Copper sulphide did not distribute in the system water-ether-alcohol. (*Jour. Phys. Chem.* 12, pp. 706-716, 1908).

No. 3. *W. Lash Miller*:—*The theory of the direct method of determining transport numbers.* The impression has gained ground among experimental workers in this field, that "directly" determined transport numbers need not necessarily agree with those determined by Hittorf's method. The theory of the direct method was first developed by Kohlrausch from equations involving the mobilities of the ions concerned; it is possible, however, to avoid all reference to rates, mobilities, current and other functions involving time, and to shew that transport numbers properly calculated from observations of the movement of the meniscus must be identically the same as those obtained from the analytical method; in fact, that the meniscus method is but a modification of the method of Hittorf, in which the amounts of the various constituents of the solution transported are determined by volume measurements instead of by quantitative chemical analysis. (*Zeit. phys. Chem.* 69, pp. 436-441, 1909).

No. 4. *J. D. Barter*:—*The sulphates of barium.* Freshly precipitated barium sulphate was washed several times with sulphuric acid and

finally shaken with sulphuric acid of various concentrations for four weeks, when the liquids and moist solids were analysed. The composition of the pure solids was determined from these analyses by the graphic method. Besides the ordinary sulphate BaSO_4 , a compound of the composition $3\text{BaSO}_4 \cdot 8\text{SO}_3 \cdot 7\text{H}_2\text{O}$ was indicated, stable in contact with acids of composition varying from 69.8 % to 75.5% of sulphur trioxide. The crystals were very minute, but appeared under the microscope to be tetragonal. A third compound consisting of fine silky needles, the twinning of which seemed to indicate that they were rhombic, was obtained in contact with strong acids. The formula of this compound was uncertain, but is approximately $4\text{BaO} \cdot 5\text{SO}_3 \cdot 6\text{H}_2\text{O}$. (Winter, 1908-9).

No. 5. L. T. Acton:—*Catalytic action of ether on the oxidation of arsenious acid by air.* In connection with measurements of the distribution of arsenious acid between ether and water, Mr. Acton observed that the oxidizing action of dissolved air on arsenious acid is greatly accelerated by the presence of a little ether. The reaction is not instantaneous, but is quick enough to vitiate analytical determinations made in the ordinary way. (Winter, 1909-10).

No. 6. J. S. Laird:—*The toxicity of solutions containing phenol and salts.* A number of measurements of the rate of poisoning by phenol solutions containing salts were made with anthrax and with micrococcus pyogenes aureus; and the distribution of the phenol between the salt solutions and purified petroleum was determined. In the case of the anthrax, relatively strong phenol solutions were used and the results agreed with the theory set up by Lash Miller and Mackenzie (*these Transactions*, Vol. IX, Sec. III p 51). With micrococcus however, an observation made the year before by Dr. W. S. Lemon was confirmed, viz:—that very weak phenol solutions are rendered less toxic by addition of salt. It was found that salt solutions isotonic with such dilute phenol solutions are themselves poisonous; thus in experimenting with susceptible microbes "osmotic" poisoning may be superadded to the action of the toxic agent.

Finally the distribution ratio was determined for each of the eleven solutions (containing phenol and various salts) whose relative toxicity had been determined by Paul and Krönig; and in every case the toxicity of the solution was found to run parallel to the chemical potential of the dissolved phenol. (Winter, 1909-1910).

No. 7. D. A. Welsh:—*Electrolysis of solutions containing ferric salts and potassium iodide.* If a cathode is introduced into a solution in which ferric chloride is being slowly reduced by potassium iodide, the electromotive force thermodynamically "necessary" to reduce the ferric salt is obviously less than that needed to reduce the free iodine

liberated by the reaction. Mr. Welsh's experiments shewed, however, that in point of fact iodine and not ferric salt is reduced. This result has an important bearing on the theory of electrolytic reduction of ferric salts; it led to the experiments of Burt-Gerrans described below. (Winter, 1909-1910).

No. 8. *T. R. Rosebrugh and W. Lash Miller:—Mathematical theory of the changes of concentration at the electrode brought about by diffusion and by chemical reaction.* Owing to the chemical changes which accompany electrolysis, the composition of the electrolyte at the electrodes is different from that in the body of the solution. Diffusion currents are consequently set up which tend to remove these differences; and if convection be avoided, the concentration of any constituent at any point in the solution will depend only on the initial composition of the solution, and on the amounts which have been carried to or from the electrodes by diffusion and by electrolytic migration.

In the simpler cases, at all events, these changes of concentration are susceptible of mathematical treatment; Weber and Sand have considered the case of electrolysis with constant currents, and Warburg has deduced an equation for the stationary state on electrolysis with a sinusoidal current through a diffusion layer of "infinite" length. The present paper deals with the whole problem in a systematic manner, and includes the discussion of electrolysis with intermittent, successive, and sinusoidal currents, without restrictions as to the duration of the electrolysis or the length of the column of liquid through which the diffusion takes place. The increasing application of the oscillograph to the study of instantaneous conditions at the electrode, led us to pay particular attention to the changes which take place within the first fraction of a second after throwing on the current, while Richards' work on electrolysis with alternating currents, followed by the interesting experiments of LeBlanc and of Reichenstein with copper electrodes in cyanide solutions, induced us to include the case of non-instantaneous chemical reactions between the primary products of electrolysis and the other constituents of the solution. Experimental methods are suggested by which, in suitable cases, the velocity constants of such reactions might be determined. (*Jour. Phys. Chem.* 14, pp. 816-884, 1910).

No. 9. *W. H. Eastlake:—Distribution of acetic and succinic acids between water and solutions containing two organic liquids.*—Measurements of the distribution of any analytically determinable substance between two immiscible solvents furnish a means of determining the effect of concentration on the chemical potential of the given substance in one of the solutions if it is known for the other.

This method has been applied hitherto only where both solvents were chemical compounds; as ether, water; chloroform, water, etc. It is, however, equally applicable when one or both of them is a solution; so that a good set of distribution measurements would show the effect of the percentage of ether, say, in an ether-benzene solution on the polymerization or dissociation of acetic acid etc., dissolved in the solution of ether and benzene. Mr. Eastlake's measurements established the feasibility of the method, but were interrupted before a complete set of data had been obtained. (*Winter 1910*).

No. 10. *H. A. G. Willoughby*:—*The sulphates of calcium*. The sulphates of calcium stable at ordinary temperature in contact with sulphuric acid solutions of various concentrations were investigated by a method similar to that used with the ferrous sulphates (*see Frank B. Kenrick, above*), partial separation of the solid phases being effected by centrifuging through a loosely fitting glass valve in a tube closed by a ground-glass stopper. The extreme slowness with which equilibrium was established made a complete investigation impossible, and renders some of the results somewhat doubtful.

The following compounds were identified:—

CaSO_4 :—stable with solutions containing less acid than corresponds to the formula $\text{SO}_3 \cdot 2.1 \text{H}_2\text{O}$. The crystals were very minute, and the consequent difficulty in separating them from the viscous mother-liquor made the determination of an upper limit of the acid concentration unreliable.

$2\text{CaSO}_4 \cdot \text{H}_2\text{SO}_4$:—consists of coarse irregular granules, some of which appeared to be fragments of rhombic plates. It exists with liquids ranging from about $\text{SO}_3 \cdot \text{H}_2\text{O}$ to $\text{SO}_3 \cdot 2.1 \text{H}_2\text{O}$.

$\text{CaSO}_4 \cdot \text{H}_2\text{SO}_4$ (?):—Observed under the microscope in a drop of the mother-liquor, this substance appeared as irregular granules intermixed with small prisms, probably triangular in section. Exposed to the air it changes to a mass of very fine granules. Its range of existence is practically that of the $2\text{CaSO}_4 \cdot \text{H}_2\text{SO}_4$. No conclusive evidence was obtained as to which of these two is the stabler form.

$\text{CaSO}_4 \cdot 3\text{H}_2\text{SO}_4$:—This was not obtained pure, but was observed as fairly large transparent crystals mixed with a fine-grained paste of extremely fine granules in an acid of approximately the composition $\text{SO}_3 \cdot 0.94 \text{H}_2\text{O}$. Some of these crystals were picked out and analyzed, giving results pointing to the formula assigned; they retain their transparency for some minutes when exposed to the air, and then slowly disintegrate into fine granules.

The solubility of these calcium sulphates in the acid liquids was in every case small, but increased with increase in the concentration of the acid. The highest value obtained was for a liquid in equilibrium

with $\text{CaSO}_4 \cdot 3\text{H}_2\text{SO}_4$, which contained SO_2 : $0.94\text{H}_2\text{SO}_4 \cdot 0.07\text{CaO}$ (Winter, 1910-1911).

No. 11. W. D. Bonner:—*Experimental determination of binodal curves, plait-points, and tie-lines, in fifty systems, each consisting of water and two organic liquids.*—As it was desired to study as many different systems as possible, and as organic liquids are in general costly, it was necessary to develop a method of working which would not necessitate the use of more than a few grams of material in each experiment. The difficulties of analysis were avoided by adopting a modification of Bancroft's method of "quantitative synthesis," and the positions of the tie-lines and plait-points were determined by a graphic method described in the paper by Lash Miller and McPherson referred to above. (*Jour. Phys. Chem.* 14, pp. 738-789, 1910).

No. 12. W. W. Evans:—*The rate of propagation of flames.*—The rate at which a flame spreads along a circular wick moistened with a combustible liquid was determined by measuring the rate at which a disc of millboard (dipping in the liquid) must be rotated in order that the flame may remain stationary. For a standard size of flame, occupying a fixed position on the wick, the rate was found to be a linear function of the initial temperature of the liquid.

Curves were obtained for 22 pure liquids and solutions, with "seconds per revolution" as ordinates, and initial temperatures as abscissæ. All showed a slight concavity, most marked at temperatures near the flash-points. (Winters 1910-1912).

No. 13. Saul Dushman:—*The behaviour of copper anodes in chloride solutions.*—Having found that it was possible to make copper dissolve anodically in hydrochloric acid wholly as cupric or wholly as cuprous salt or as a mixture of these in any desired proportions depending on the concentration of acid, current density, rate of stirring and rate of circulation of the electrolyte through the cell, a series of quantitative measurements was undertaken to see whether there was equilibrium at the electrode between the cupric salts, cuprous salts, hydrochloric acid, and metallic copper.

As the concentrations at the electrode were very different from those in the body of the solution—sometimes they were twenty times as great—they had to be calculated from the latter by allowing for diffusion, and methods had to be devised for obtaining the constants needed in these calculations.

Electrolyses were carried out in which the concentration of the hydrochloric acid, the current, the anode area and the rate of circulation of the electrolyte through the cell were varied; the fraction of the copper dissolved as cuprous salt varied from 25% to 74 %, and agreed within the experimental errors with the fraction calculated

on the assumption of equilibrium, using Bodländer and Storbeck's value for the equilibrium constant. (*Jour. Phys. Chem.* 14 pp. 885-908, 1910).

No. 14. W. L. Argo:—*The velocity of sound in nitrogen dioxide gas.*—The relation between the pressure, temperature and density of nitrogen peroxide is satisfactorily expressed by the statement that there is equilibrium between two gases with formula weights corresponding to N_2O_4 and NO_2 . Up to the present no experiments have indicated that any appreciable time is required for establishing equilibrium after an alteration of pressure. The object of Mr. Argo's investigation was to ascertain whether, in extremely rapid changes of pressure, any evidence of incomplete equilibrium could be obtained.

Since the peroxide dissociates according to the equation



the adiabatic changes of pressure due to stationary sound waves will cause local dissociation and association. The actual behaviour of the gas under such changes of pressure will conform to a condition which lies between those represented by the two following limiting assumptions, viz:—(a) that the dissociation is so rapid that complete equilibrium exists at every moment in spite of the sound waves, and (b) that the rate of dissociation is so small that no change in dissociation takes place during the rapid change of pressure.

The change of density with pressure, $d\rho/dp$, may be calculated for each of these two assumptions and compared with the actual value found experimentally from the velocity of sound in the gas.

Since nitrogen peroxide attacks rubber and many metals, a modification of Kundt's apparatus for determining the velocity of sound had to be devised. An apparatus was constructed entirely of glass and platinum, and graphite powder was used for producing the dust figures. The only two experimental results obtained up to the present, gave a value for $d\rho/dp$ lying between those calculated from the assumptions (a) and (b) above. It seems probable, therefore, that the reaction between the two forms of the peroxide is not instantaneous.*

It is proposed to continue these measurements, and to determine if possible whether traces of water vapour have any effect on the rate. (Winter 1911-1912).

*Since this article was sent to press Mr. Argo has completed the investigation. The results show definitely that the rate of dissociation is so great that there is no appreciable "lag" in the reaction following changes of pressure caused by the sound waves, in the case of both dry and moist nitrogen peroxide.

The results will appear shortly in *The Journal of Physical Chemistry*, Vol. 18

No. 15. *J. T. Burt-Gerrans*:—*The electrolysis of acid solutions of copper sulphate with alternating current.*—Mr. Redman's work (*These Transactions Vol. II, Sec. III p. 244*) having shewn the applicability of the equations deduced by Rosebrugh and Lash Miller (see above) to the electrolysis of solutions of copper sulphate in maximum conducting sulphuric acid, Mr. Burt-Gerrans undertook a similar study with alternating current, using a Siemens and Halske oscillograph, and inferring the concentrations at the electrode from the voltage curves. In every case he found that the reduction of concentration by the alternating current—whether with pure sine current or with direct current superposed—was less than that calculated from the mathematical theory. As, however, experiments with interrupted direct current gave results at the cathode in fair agreement with the calculations, a study of the anodic behaviour of copper in this solution seems needed to clear up the situation. (*Winter 1911-1912*).

No. 16. *H. P. Corliss*:—*The distribution of colloidal arsenious sulphide between the two phases in systems containing ether, water, and alcohol.*—In continuation of the work of Lash Miller and McPherson, and of Bonner, referred to above, Mr. Corliss made accurate determinations of the binodal curve and tie-lines for the system water-ether-alcohol at 0°C, and quantitative measurements of the distribution of arsenious sulphide between the two phases. The results, as in all work with colloids, depend largely on the age of the colloid, the order of mixing the reagents, etc., and, as was to be expected, the distribution became less equal as the tie lines receded from the plait-point. They shew clearly, however, when standard conditions are adhered to, that within a wide range the distribution of the colloid is fairly independent of the concentration of the arsenious sulphide; and furnish the first instance in which an equilibrium of this kind has been followed out. (*Winter 1911-1912*).

No. 17. *Chas. G. Fraser*:—*Improvement in the technique of toxicity experiments.*—The experience of Mr. Laird and of others who have worked here on the rate at which microbes succumb to phenol solutions and other poisons, shews clearly that the chief experimental difficulty in carrying out such experiments lies in the lack of some quickly applicable criterion of death. To find out how many micrococci, for instance, have been killed in a given culture, it is customary to pour gelatine or agar plates and to wait a couple of days until those surviving grow into colonies large enough to count. In many instances the results only shew that either all or none have deceased, and that the work must be done all over again.

To overcome this difficulty, Mr. Fraser has developed a technique involving staining and examination under the microscope, which

enables the percentage of deaths to be ascertained with fair accuracy by a few minutes' work; plates can then be poured if needed, with the certainty that none will be wasted; or microphotographs may be made and counted at leisure. The time needed for a given poison to make a yeast cell stainable is a little longer than that required to destroy its power of reproduction; the nature and extent of this difference are now being studied. (Winter 1911-1912).

No. 18. *W. Lash Miller*:—*The chemical philosophy of the High-school text books.*—Hand in hand with the study of chemical equilibrium, the idea of continuity between chemical and "physical" changes has entered chemistry, and is transforming it. The high-school text-books, however, as a class, in their tendency deny this continuity *in toto*. In order to be "up to date," however, they include much of the experimental evidence which has forced this conception into the science, with the result that they contradict themselves, and involve the whole subject in a maze of vagueness and mystification wholly foreign to the scientific spirit.

Numerous illustrations are given, and the importance of a change is insisted upon. At present, children are being trained to accept obscure, equivocal, and dogmatic statements in place of clear and exact thought, and high-school "chemistry" is fast earning a place among that group of pedagogic processes which Huxley characterized as the "direct and preventable cause of most of the world's stupidity."*

No. 19. *J. C. McRae*:—*The distribution of temperatures during the solidification of undercooled liquids.*—By means of a fine thermocouple and a quick-acting oscillograph, the temperatures in a supercooled solution were measured at different distances in front of an advancing column of crystals. When the crystals once reached the wire, of course, the temperature remained stationary until the solidification was complete. A differential equation was set up to describe the temperature distribution. (Winter 1911-1912).

No. 20. *W. B. Wiegand*:—*The effect of an external heat source on the rate of propagation of flames.* Mr. Evans' experiments (see above) were checked and amplified by studying the effect of heat supplied by a gold wire heated by a measured current and held at fixed distances in front of the flame. Platinum could not be used because of its catalytic action. (Winter 1911-1912).

No. 21. *Frank B. Kenrick*:—*Lantern experiments on reactions in non-homogeneous systems.*—(i) Working model of the "piston and cylinder" used in thermodynamic argumentation; the main difficulty was in making an air-tight frictionless joint between the piston and the cylinder. This was overcome by a mercury packing, kept in place by surface tension. (ii) Modification of the above to shew the proper-

**Science*, 34, 257-263 (1911).

ties of a liquid in equilibrium with its vapour. (iii) Simpler form of apparatus for working at atmospheric pressure. (iv) Decomposition temperature of calcium-chloride-ammonia (v) Delayed reactions supersaturation, etc. (*Jour. Phys. Chem.* 16, pp. 519-526, 1912).

No. 22. *Frank B. Kenrick*:—*Some lecture experiments on surface tension.*—(i) Mechanical model, shewing surface tension balanced by a movable weight. (ii) Two drops, analogous to the well-known experiment with large and small soap bubbles. (iii) Surface tension and solubility; optical device to shew the difference in solubility between coarse and fine gypsum powder. (iv) Surface concentration in saponin solution; shews that a freshly formed surface of saponin solution has practically the same surface tension as pure water. (v) Surface concentration of methyl violet solution; the foam has a different composition to that of the body of the solution, shewn by double cell in lantern. (vi) Oil films and water; (*Jour. Phys. Chem.* 16, pp. 513-518, 1912).

No. 23. *W. Lash Miller*:—*The influence of diffusion on the electromotive force produced in solutions by centrifugal action.* In Tolman's account of his measurements of the electromotive force produced in solutions of potassium iodide and free iodine by centrifugal action, the equations were deduced without allowing for any possible differences in concentration at the two ends of the tube produced by the whirling. As, in some of his experiments, these differences would become very considerable if the rotation were sufficiently prolonged, it seemed possible that even in a few minutes the "concentration cell" effect might become measurable, and that it might perhaps account for the "residual electromotive force" observed by him.

The calculations shewed, however, that the polarization produced by concentration changes in short periods of centrifuging was very slight; as it chanced that the effects produced by the iodine and the iodide almost neutralized one another.

As no previous attempt has been made to calculate the rate at which diffusion would take place under the influence of centrifugal force, the assumptions made in the calculation are being checked in this laboratory. (*Trans. Am. Electrochem Soc.* 21, pp. 209-217, 1912).

No. 24. *J. T. Burt-Gerrans*:—*Electrolysis of solutions containing free iodine and potassium iodide together with chromic, arsenic, or arsenious acid.* These experiments, carried out with students in the electrochemical laboratory, were suggested by the work of Mr. Welsh, above. They shew that in solutions containing chromic or arsenic acids, the iodine instead of the acid, is reduced by a cathode, while in solutions where arsenious acid is being oxidized by iodine an anode oxidizes the potassium iodide instead of the arsenic. Experiments with similar

results were carried out by placing electrodes in solutions where iodide and iodine were in equilibrium with ferric and ferrous salts, or with arsenic and arsenious acids. (Winter 1912-1913).

No. 25. *K. E. Burgess*:—*The toxicity of solutions containing phenol and sodium benzoate.* Using the stain method (referred to under Mr. Fraser's name above) as a guide, Mr. Burgess studied the effect of pure water, sodium benzoate solutions, and solutions containing both phenol and sodium benzoate on *micrococcus pyogenes*. His results furnish a satisfactory confirmation of the explanation given above (see *Laird*) for the "abnormal" effect of salts in very dilute phenol solutions. (Winter 1912-1913).

No. 26. *N. J. Ireland*:—*The nature of the cathodic silver deposit.* A series of microphotographs were made of the silver deposited from silver nitrate solution, with different current densities, concentrations, temperatures, and rates of stirring. Preliminary determinations of the "limiting current" made it possible to plan the experiments so that each differed from the next in one respect only, e.g., either in concentration at the electrode, or in current density, not in both together, as has been the case in previous work. (Winter 1912-1913).

No. 27. *Frank B. Kenrick and R. L. McGregor*:—*Thickness of the surface layer in solutions of surface active substances.* From the change of the surface tension with the concentration of a dilute solution it is possible to calculate, by Gibbs' equation, the "surface accumulation" of dissolved substance per unit area of surface. If the concentration of the dissolved substance in the surface layer were known and if an assumption were made as to the law according to which the concentration changes in a direction normal to the surface, the order of magnitude of the thickness of the surface layer could be calculated. In order to obtain information as to the concentration of the surface layer, some property of that layer must be measured, and the value compared with the corresponding values for solutions of known concentration.

Two properties suggested themselves as suitable for this purpose:—(i) the surface tension of the liquids, (ii) the critical angle of reflection, from which it was hoped the refractive index of the surface layer might be obtained. A measurement of the surface tension of the liquid by one of the static methods gives the value of this property for the surface layer of composition corresponding to equilibrium; while the determination of the surface tension by the oscillating jet method gives the value of this property when the composition of the surface approaches that of the body of the liquid, whose concentration is known. It was hoped that a comparison would lead to an estimate of the concentration of the surface layer.

Mr. R. L. McGregor undertook this part of the experiments. The measurements with the jet proved to be unexpectedly difficult, and Mr. McGregor was compelled by illness to discontinue his work before final results were obtained. (*Winter, 1912-1913*).

No. 28. *R. T. Elworthy:—The critical angle of reflection from solutions of surface active substances.* The measurements of the critical angle referred to above were carried out by Mr. Elworthy, and although the results are disappointing, in so far as they do not shed much light on the problem for the solution of which they were undertaken, they are quite definite. Aqueous solutions of amyl alcohol, phenol, aniline, and propionic acid were investigated.

The measurements were made by observing, through a Nicol, the image of a uniformly illuminated slot, about 2 cm. long, reflected from the surface of the solution. The Nicol was held at the end of a movable wooden arm, which was adjusted until the black spot seemed equidistant from the upper and lower end of the slot. In every case the critical angle gave a refractive index for the surface layer only slightly different from that calculated (and determined by Pulfrich's refractometer) for the body of the liquid. The slight deviation from this value, was, it is true, in the direction to be expected from the assumption of an accumulation of solute in the surface, but its magnitude suggests another interpretation of the results, viz:—that the surface layer is too thin to give the true value of the refractive index from the critical angle of reflection. (*Winter 1912-1913*).

No. 29. *W. J. Fawcett:—Rate of solution and crystallization of gypsum.* A crystal of gypsum was protected with wax so that only 3 cm.² of a freshly cleaved surface was exposed. This was rotated in unsaturated and supersaturated solutions of gypsum, the concentration of the liquid being determined at intervals by conductivity measurements. The supersaturated solution was prepared by shaking a solution with finely ground gypsum and rapidly filtering through macerated filter paper until the liquid was almost optically empty. A striking difference was noted in the behaviour of the unsaturated and the supersaturated solutions. In the former the concentration increased rapidly, with decreasing velocity, until the normally saturated solution was produced. In the case of the supersaturated solution, on the other hand, a comparatively rapid separation of gypsum appeared to take place at first, followed by an almost stationary condition in which no appreciable change in concentration occurred during a week's stirring, although the solution was as much as 10% supersaturated. The same phenomenon was observed with a solution 6% supersaturated. In neither case could any change in the smoothness of the crystal be detected with the microscope. Whether the stationary condition is

brought about by a change in the crystal or in the solution has not yet been definitely settled. (*Winter, 1912-13.*)

No. 30. *W. J. Fawcett:—The absence of supersaturation of liquids in liquids.* In connection with the peculiar results found for the rate of solution of gypsum (See No. 29 above) it was thought that by investigating the rate of solution and precipitation in the case of a solution of a liquid in a liquid, where the complicating factors of solidity and crystal form were excluded, some explanation of the behaviour of gypsum might be reached. Here the unexpected difficulty was encountered that even slightly supersaturated solutions could not be prepared. This fact is established by the following experiments.

A nearly saturated solution of one liquid in another was sealed up in a tube of thin glass. This was clamped in a glass thermostat parallel with a similar tube containing a slightly weaker solution to serve as a blank for comparison. The apparatus was encased in a black cloth, a beam of light being admitted through a slit in the side. The tubes were observed endwise through two small holes in the front. The temperature of the bath could be changed or kept constant to within 0.1°C . The temperatures at which turbidity appeared and at which it vanished were compared for solutions of phenol in water, valeric acid in water, aniline in water, chloroform in water with alcohol, ether in water with alcohol. In every case the temperature at which the turbidity disappeared was higher by one or two tenths of a degree than the temperature of precipitation, but the difference was of the order of magnitude of the experimental error, the slight permanent opalescence observed in all liquids making accurate readings difficult. Since it was thought that suspended particles might act as nuclei for the precipitation of the liquids, several methods were tried for freeing the solutions of these suspensions. Neither filtering through macerated filter paper nor repeated precipitation and removal of the precipitated liquid, even when this was carried out without exposure to the air, led to any increase in the tendency of the liquids to form supersaturated solutions. (*Winter, 1912-13.*)

No. 31. *W. H. Martin:—The Tyndall effect in liquids.* All liquids show more or less opalescence when traversed by a bright beam of light. Experiments were undertaken with a view to finding out to what extent this opalescence could be removed by various methods of purification. The following methods were investigated:

(a) Repeated distillation, in vacuo, in an all-glass apparatus, without ebullition. Various kinds of glass were used.

(b) Fractional distillation in vacuo, with the same precautions as in (a).

(c) Envelopment by precipitation of the hydroxides of aluminium, zinc and cadmium, and by colloidal arsenic sulphide.

(d) Cataphoresis.

The general result was that the light beam in water and in aqueous alcohol—the two liquids most thoroughly investigated—consists of two parts; a part which is removed by each of the methods of purification and a part which is not removed by any of the methods and which is *constant in intensity irrespective of the method of purification used*. This permanent part is faint and is plane-polarized, and can be seen only if the room is dark, the light beam very intense, and the vessel clean and free from striæ.

The intensity of the permanent opalescence of water was not affected by change of temperature. It was also unaltered by the addition of hydrofluoric acid and is therefore not due to silica.

A sample of water, purified by method (a), was cooled in a tube 2 mm. in diameter to -26°C before it froze. Ordinary distilled water under the same conditions froze at -11°C . (*Winter 1912-1913*).